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## (54) MANUFACTURE OF METAL MAGNETIC POWDER

## (57)Abstract:

PURPOSE: To notably enhance the oxidation resistance of the metal magnetic powder by performing surface oxidizing step using a low oxygen concentration gas containing steam in specific concentration at specific temperature.

CONSTITUTION: As for a metallic oxide mainly comprising iron, a spinel compound having no dehydrating hole at all bored by heating step in an inert gas atmosphere after particle surfaces are coated with a mixture layer containing at least dihydric transition metallic compound is used. Next, a metallic iron produced by reducing this metallic oxide using a reducing gas is surface oxidized. As for this oxidizing step, the reduced metallic iron is oxidized at the temperature of 60-120°C in an inert gas containing moisture content at the partial steam pressure of 20-50mmHg and 100-2500ppm of oxygen. This surface oxidizing step, despite a simple one, can notably enhance the oxidation resistance thereby enabling the manufacturing method of metal magnetic powder having excellent magnetic characteristics to be devised.

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**CLAIMS**

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[Claim(s)]

[Claim 1] The manufacture approach of the metal magnetism powder characterized by to be what oxidizes at the temperature of 60-120 degrees C in the approach of returning the metallic oxide which makes iron a subject by reducibility gas, carrying out scaling processing of the metal iron obtained, and manufacturing metal magnetism powder, in the inert gas with which scaling processing contains the moisture of the steam partial pressure 20 - 50mmHg, and 100-2500 ppm oxygen for the metal iron after reduction.

[Claim 2] The manufacture approach according to claim 1 which is the spinel compound which is heated and obtained by the inert atmosphere after the metallic oxide which makes iron a subject covers the mixture layer which contains a divalent transition-metals compound at least on the particle front face of the water iron-oxide particle of a needle shape crystal, and with which a dehydration hole does not exist substantially.

[Claim 3] The manufacture approach according to claim 2 which is the layer which the mixture layer which contains a divalent transition-metals compound at least turns into from a cobalt compound, a silicon compound, and/or an aluminium compound.

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[Translation done.]

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Industrial Application] About the manufacture approach of the metal magnetism powder used for magnetic recording, in more detail, this invention returns a metal powder precursor and relates to the approach of manufacturing the oxidation-resistant outstanding metal magnetism powder, by using the hypoxia concentration gas which includes the scaling stabilization after metal-izing for the steam of specific concentration, and carrying out in a specific temperature requirement.

[0002]

[Description of the Prior Art] Although development of various kinds of recording methods has a remarkable thing in recent years, the advance of the formation of small lightweight of a magnetic recorder and reproducing device is remarkable especially. Along with this, the demand of high-performance-izing to magnetic-recording media, such as a magnetic tape and a magnetic disk, is becoming large.

[0003] In order to satisfy such a demand to magnetic recording, the magnetic powder which has high coercive force and high saturation magnetization is required. Although the so-called cobalt content iron oxide which generally denaturalized needlelike magnetite, maghemites, or these magnetic-oxide-of-iron powder with cobalt as magnetic powder for magnetic recording is used conventionally, in order to obtain the medium of high power more, the so-called metal magnetism powder is beginning to be used in the end with higher coercive force and saturation magnetization of a ferromagnetic metal powder.

[0004] As the manufacture approach of such metal magnetism powder, although various approaches are proposed, the approach of heating the iron-oxide particle obtained from an economical predominance by generally carrying out heating dehydration of needlelike goethite or this needlelike in reducibility gas ambient atmospheres, such as hydrogen, and returning even to metal iron is used.

[0005] However, a big problem exists in the metal magnetism powder obtained by doing in this way. That is, metal magnetism powder has the fault that it is chemically unstable and saturation magnetization decreases with the passage of time. Solution of this fault is variously benefited for the proposal, for example, although scaling (for example, JP,59-16901,A, JP,59-170201,A) in the inside of a solvent and the approach (JP,1-21002,A) of oxidizing while changing temperature into a multistage story in a gaseous phase are proposed, still sufficient engine performance is not obtained. Moreover, although the approach (JP,60-26602,A) of oxidizing at an elevated temperature (200-600 degrees C) is also proposed using a steam together, since degradation of a static magnetism property arises so that it may state later, it cannot be said to be a desirable approach.

[0006] That this technical problem should be solved, oxidation resistance is sharply improved by simple scaling processing, and the purpose of this invention is to offer the manufacture approach of metal magnetism powder of excelling also in magnetic properties.

[0007]

[Means for Solving the Problem] In order to attain the aforementioned purpose, as a result of considering oxidation stabilization of the metal magnetism powder which returned and obtained the metallic oxide which makes iron a subject, by performing scaling processing at specific temperature using the hypoxia concentration gas containing the steam of specific concentration, this invention persons found out that the oxidation resistance of metal magnetism powder was sharply improvable, and resulted in completion of this invention.

[0008] That is, it be relate with the manufacture approach of the metal magnetism powder characterize by for the summary of this invention to be what oxidize at the temperature of 60-120 degrees C in the approach of return the metallic oxide which make iron a subject by reducibility gas, carry out scaling processing of the metal iron obtain, and manufacture metal magnetism powder, in the inert gas with which scaling processing contain the moisture of the steam partial pressure 20 - 50mmHg, and 100-2500 ppm oxygen for the metal iron after reduction. Moreover, in the manufacture approach of this invention, after the metallic oxide which makes iron a subject covers the mixture layer which contains a divalent transition-metals compound at least on the particle front face of the water iron-oxide particle of a needle shape crystal, if the spinel compound which is heated and obtained by the inert atmosphere and with which a dehydration hole does not exist substantially is used, especially the effectiveness of this invention is effective.

[0009] There is especially no limit that the axial ratio of the metallic oxide which makes a subject the iron used for this invention, and magnitude should just be what is generally usually used as a raw material of metal magnetism powder. Furthermore, even if various metallic elements are included for amelioration of control of magnetic properties, or the property of dispersibility and others, it does not interfere. The approach which the well-known reduction generally used is applied, for example, keeps the reduction to the metal of the metallic oxide which makes iron a subject at 350-550 degrees C in a hydrogen air current for 2 hours or more is mentioned.

[0010] In order that activity may be strong and the obtained metal powder may tend [ very ] to receive oxidation, the following scaling processings are performed by the manufacture approach of this invention. That is, the scaling art in this invention is performed by usually leading the inert gas containing the moisture of the steam partial pressure 20 - 50mmHg, and 100-2500 ppm oxygen, and the inert gas containing the moisture of the steam partial pressure 20 - 50mmHg and 200-500 ppm oxygen is used preferably. The effectiveness of containing a steam, if a steam partial pressure is lower than 20mmHg(s) is no longer seen, and if higher than 50mmHg, oxidation resistance will serve as a defect on the contrary. Moreover, if 2500 ppm is exceeded, it will think for local generation of heat, but since the fall of magnetic properties takes place, an oxygen density is not desirable. Although there is especially no big problem when an oxygen density is low, time amount until it obtains the oxide film of predetermined thickness becomes long, and about 100 ppm is considered to be a minimum from the field of workability.

[0011] Furthermore, the oxidation temperature at the time of oxidizing is also important, and it is usually necessary to perform 60-120 degrees C at 70-90 degrees C preferably. That is, it is for problems, such as it becoming difficult to maintain a predetermined steam partial pressure by dew condensation within piping etc., if temperature is too low, the effectiveness of a coexistence steam becoming inadequate if too conversely high, and being hard to acquire sufficient oxidation resistance, and being accompanied by the fall of



magnetic properties, to occur. What is necessary is just to make it the difference of an outlet oxygen density and an inlet-port oxygen density set to about 30 ppm or less that the time amount of processing should just set up time amount until scaling will not progress substantially, although based also on an inlet-port oxygen density. What is necessary is generally, just to carry out for about 30 hours, when the conditions of 250 ppm of oxygen densities perform at 70 degrees C. Thus, although the scaling art in this invention is a simple approach, oxidation resistance is improved sharply.

[0012] In the manufacture approach of this invention, although the case where it is the spinel compound which is heated and obtained by the inert atmosphere and with which a dehydration hole does not exist substantially is more desirable after the metallic oxide which makes iron a subject covers the mixture layer which contains a divalent transition-metals compound at least on the particle front face of the water iron-oxide particle of a needle shape crystal, such a spinel compound can be obtained as follows.

[0013] As a divalent transition-metals compound, Co, Fe, Zn, Cu, Cr, nickel compound, etc. are mentioned, and it is not restricted especially. The layer which consists of mixture of three sorts of compounds of the layer which well-known compounds, such as silicon, aluminum, tin, and a titanium compound, are usually used, for example, consists of mixture of a cobalt compound and a silicon compound as other compounds which constitute a mixture layer with a divalent transition-metals compound, the layer which consists of mixture of a cobalt compound and an aluminium compound or a cobalt compound, a silicon compound, and an aluminium compound is mentioned.

[0014] In the mixture layer containing a divalent transition-metals compound, the divalent transition-metals compound is usually preferably contained 7 to 20% 3 to 25% as a weight ratio to the iron atom in goethite. This is because a desired property is no longer acquired even if there are too many amounts of divalent transition metals and it is too few. Moreover, silicon and aluminum atoms, such as other compounds which constitute a mixture layer, for example, a silicon compound, and an aluminium compound, usually contain 0.5 - 1% preferably 0.2 to 2% as a weight ratio to the iron atom in goethite similarly. Moreover, the Shigekazu Harako ratio of a divalent transition-metals compound and other compounds which constitute a mixture layer is usually 10:1 to 20:0.5.

[0015] The approach of forming the mixture layer containing such a divalent transition-metals compound in a needlelike water iron-oxide particle front face is performed by the well-known approach used for deposition, such as a deposit of the insoluble matter from a solution condition, and a colloid compound, etc. In order to make the layer which consists of mixture of a cobalt compound and a silicon compound form as the example In order to make the layer which makes pH of a system the seven neighborhoods in a cobalt sulfate water solution after adding a No. 3 cay sow, and consists of mixture of a cobalt compound and an aluminium compound form After carrying out simultaneous adding of an aluminum-sulfate water solution and the cobalt sulfate water solution, pH of a system is made into the seven neighborhoods in an alkali water solution. Moreover, in order to make the layer which consists of mixture of three sorts of compounds, a cobalt compound, a silicon compound, and an aluminium compound, form pH of a system is set to 7 in cobalt sulfate and an aluminum-sulfate water solution after adding a No. 3 cay sow. Acid water solubility compound water solutions, such as a sulfate, are added to the slurry of goethite, and the method of depositing an insoluble oxide thru/or a hydration oxide is usually mentioned by subsequently adjusting pH of a system with an alkaline water solution, such as setting pH of a system to 10 in an alkali water solution after that.

[0016] The spinel compound said by this invention is an oxide mainly concerned with the iron oxide, and what [ its ] has the main peaks of an X diffraction is in a spacing  $2.97 \pm 0.05$ ,  $2.53 \pm 0.05$ , and the location equivalent to  $2.10 \pm 0.05 \text{ \AA}$  very.

[0017] Although it will generally become easy to produce a dehydration hole if heating dehydration of the goethite is carried out in air, this dehydration hole is observable with an electron microscope. Since correlation is regarded as the specific-surface-area value of a particle and the existence of a dehydration hole which were measured by fluid type specific-surface-area automatical measurement equipment (flow SOBU2300 form, Shimadzu make) as an approach of judging the existence of a dehydration hole simply, the existence of a dehydration hole can be judged using the percentage reduction which can be obtained from a specific-surface-area value. Namely, the percentage reduction of the specific surface area of a particle before and after the spinel compound which is said by this invention and in which a dehydration hole does not exist substantially carries out heating-at-high-temperature processing is 10% or more of spinel compound, and, as for less than 10% of thing, a dehydration hole is seen. Percentage reduction is called for by the degree type here.

Percentage reduction = (specific surface area after specific-surface-area-heat treatment before heat treatment) specific surface area before /heat treatment [0018]

In the approach of this invention, in order to make such a spinel compound with which a dehydration hole does not exist substantially form, the water iron-oxide particle of a needle shape crystal can be easily made in an inert gas air current by carrying out heating-at-high-temperature processing of the water iron-oxide particle. This processing is made after covering the mixture layer which contains a divalent transition-metals compound at least on the water iron-oxide particle front face of a needle shape crystal as is the above. In this case, although it is not restricted especially as inert gas and nitrogen gas, argon gas, etc. are usually used, it is good to carry out in a nitrogen gas air current preferably from a cheap point.

[0019] The temperature requirement of heating-at-high-temperature processing is usually 400-700 degrees C, and is 450-600 degrees C preferably. Since it is still hematite, and it will become easy to produce a dehydration hole and a grain child higher than 700 degrees C will lifting-come to be easy of welding even if it is processing in an inert gas air current if lower than 400 degrees C, it is not desirable. Although heating time is based also on also whenever [ stoving temperature ], it is usually 1 - 2 hours preferably for 0.5 to 4 hours.

[0020] If such heating-at-high-temperature processing is performed in air as indicated by JP,63-61413,A, a spinel compound will stop at not being formed but forming the hematite with which the dehydration hole remained, and since there is a possibility that it may become impossible to obtain the metal magnetism powder which cutting arises at the time of reduction in a hydrogen air current, stops holding needlelike nature, and has the target engine performance, cautions are required.

[0021] Although the manufacture approach of this invention can use the above spinel compounds suitably, by this invention, what performed covering with other compounds further apart from the aforementioned mixture layer if needed can also be used for it. For example, since sintering between the particles of metal magnetism powder is prevented at the time of heating reduction, the deposition of the well-known compounds, such as silicon and aluminum, can be carried out to the outermost shell of a particle. The silicon compound and aluminium compound layer which are the outermost layer being independent, or especially the engine performance of metal magnetism powder that will finally be obtained if what formed the aluminium compound layer after the silicon compound stratification is used especially, although formed in the form of concomitant use of both is excellent.

[0022] Formation of the silicon in this case and/or an aluminium compound layer is 2 - 6% preferably 1 to 10% as a weight ratio of the sum total of the silicon and/or aluminum to the iron atom in goethite. The saturation magnetization of the metal magnetism powder which will be obtained if there is too more sum total of silicon and aluminum than 10% becomes rather low, and this is because it is not desirable. Moreover, it is because the effectiveness which performed these covering as an outermost layer is not acquired at less than 1%.

[0023] Thus, if it heats at 400-700 degrees C in a nitrogen air current as mentioned above by making the goethite which has the

mixture layer, silicon, or aluminium compound layer containing the obtained divalent transition-metals compound into inert gas, it can change into the spinel compound with which a dehydration hole does not exist substantially, and can use for this invention.

[0024] Manufacture of the magnetic-recording medium containing the metal magnetism powder excellent in the oxidation resistance acquired as mentioned above and magnetic properties can be performed according to a conventional method. That is, distributed mixing of this metal magnetism powder is carried out with binder resin, an organic solvent, and other need components, a magnetic coating is prepared, and this magnetic coating is applied on bases, such as polyester film, with the means of arbitration, such as a doctor blade method, the gravure method, the reversing method, and roll coating, and is performed by the approach of drying behind magnetic field orientation as occasion demands.

[0025]

[Example] Hereafter, although an example and the example of a comparison explain this invention in more detail, this invention is not restricted at all by these.

[0026] Goethite (diameter of major axis: 0.18-micrometer, axial ratio:8) 500g was distributed for about 1 hour using the equipment which prepared the circulation line which installed pipeline mold disperser my RUDA (Ebara make) in the exterior of example 1 reaction vessel in the solution which added poise 530 (Kao Corp. make) 15g (3% of opposite powder) to 10l. of ion exchange water. No. 3 cay sow (SiO<sub>2</sub> 29% per part) 17.2g was added continuing distribution by my RUDA. Subsequently, after dropping the water solution which dissolved 270g of cobalt sulfate 7 hydrates in 1000ml ion exchange water to pH6.5 and making a Si/Co mixture layer put on a front face, the remaining cobalt sulfate water solution was dropped, the 1.2 mol/l. ]-NaOH water solution was dropped, and pH was set to 10. Then, it washed until the electrical conductivity of a penetrant remover became below 100microS/cm using ion exchange water. Furthermore, the poise 530 (15g) was added, it re-distributed, No. 3 cay sow (SiO<sub>2</sub> 29% per part) 69g was added, the 1 hour after aqua fortis was dropped, pH was set to 6.5, and the silicon compound layer was made to put on this. Finally, immediately after adding 172ml of NaOH water solutions with a concentration of 2 Ns to this suspension, the water solution which dissolved sulfuric-acid band (aluminum<sub>2</sub> O<sub>3</sub> 9.3% per part) 34g in 165g of ion exchange water is dropped, and the layer of the hydroxide of aluminum was made to put, and this precipitation was rinsed, and it filtered and dried.

[0027] The particle size regulation of the metal precursor obtained as mentioned above was carried out to 48-64 meshes, and flow \*\*\*\* with a bore of 62mm performed heat-treatment at 500 degrees C for 1 hour among the nitrogen air current with a gas linear velocity of 7cm [second ]. Subsequently, it returned at 500 degrees C among the hydrogen air current for 6 hours. Aeration of the nitrogen gas of steam partial pressure 34mmHg which contains 250 ppm oxygen at 80 degrees C was carried out with the gas linear velocity of 7cm/second after reduction termination, and the front face was oxidized until the outlet oxygen density was set to 230 ppm or more. Then, it dried in nitrogen gas and the metal magnetism powder 1 which is this invention article was obtained. The property of the obtained metal magnetism powder is shown in Table 1 with other examples (examples 2-3, examples 1-3 of a comparison).

[0028]

[Table 1]

	金属磁性 粉末No	H c (Oe)	$\sigma s$ (emu/g)	$\sigma r / \sigma s$	$\sigma s'$ (emu/g)	$\sigma s' / \sigma s$ (%)
本 発 明 品	1	1600	120	0.51	115	96
	2	1610	123	0.52	116	94
	3	1600	123	0.51	116	94
比 較 品	1	1600	121	0.51	107	88
	2	1580	119	0.51	105	88
	3	1500	115	0.47	—	—

注)  $\sigma s'$  : 60℃ / 90%RH保存1週間後の $\sigma s$

[0029] After performing even reduction of a metal precursor like example 2 example 1, aeration of the nitrogen gas of steam partial pressure 34mmHg which contains 250 ppm oxygen at 70 degrees C was carried out with the gas linear velocity of 7cm/second, and the front face was oxidized until the outlet oxygen density was set to 230 ppm or more. Then, it dried in nitrogen gas and the metal magnetism powder 2 which is this invention article was obtained.

[0030] After performing even reduction of a metal precursor like example 3 example 1, aeration of the nitrogen gas of steam partial pressure 34mmHg which contains 500 ppm oxygen at 70 degrees C was carried out with the gas linear velocity of 7cm/second, and the front face was oxidized until the outlet oxygen density was set to 470 ppm or more. Then, it dried in nitrogen gas and the metal magnetism powder 3 which is this invention article was obtained.

[0031] After performing even reduction of a metal precursor like example of comparison 1 example 1, aeration of the nitrogen gas which does not contain a steam including 250 ppm oxygen at 80 degrees C was carried out with the gas linear velocity of 7cm/second, the front face was oxidized until the outlet oxygen density was set to 230 ppm or more, and metal magnetism powder (comparison article 1) was obtained.

[0032] After performing even reduction of a metal precursor like example of comparison 2 example 1, aeration of the nitrogen gas of steam partial pressure 100mmHg which contains 250 ppm oxygen at 80 degrees C was carried out with the gas linear velocity of 7cm/second, and the front face was oxidized until the outlet oxygen density was set to 230 ppm or more. Then, it dried in nitrogen gas and the metal magnetism powder (comparison article 2) which oxidized the front face was obtained.

[0033] After performing even reduction of a metal precursor like example of comparison 3 example 1, aeration of the nitrogen gas of steam partial pressure 34mmHg which contains 250 ppm oxygen at 150 degrees C was carried out with the gas linear velocity of 7cm/second, and the front face was oxidized until the outlet oxygen density was set to 230 ppm or more. Then, it dried in nitrogen gas and the metal magnetism powder (comparison article 3) which oxidized the front face was obtained.

[0034] As mentioned above, in the examples 1-3, metal magnetism powder with high coercive force (Hc) and an angle-of-elevation

mold ratio ( $\sigma_{\text{mar}}/\sigma_{\text{mas}}$ ) is obtained, and it turns out that it maintains high saturation magnetization ( $\sigma_{\text{mas}}$ ) also after saving the obtained metal magnetism powder for one week under 60 degrees C / 90%RH ambient atmosphere, and oxidation resistance is excellent. On the other hand, although magnetic properties are enough, after saving them for one week under 60 degrees C / 90%RH ambient atmosphere, its saturation magnetization ( $\sigma_{\text{mas}}$ ) is low, and as for the metal magnetism powder obtained in the examples 1 and 2 of a comparison, they are inferior in oxidation resistance. Moreover, in the example 3 of a comparison, since oxidation temperature is high, degradation of magnetic properties is seen.

[0035]

[Effect of the Invention] According to the manufacture approach of the metal magnetism powder of this invention, oxidation resistance is sharply improved by simple scaling processing, and the metal magnetism powder which is excellent also in magnetic properties can be obtained.

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[Translation done.]

# MANUFACTURE OF METAL MAGNETIC POWDER

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## Abstract of JP6069011

**PURPOSE:** To notably enhance the oxidation resistance of the metal magnetic powder by performing surface oxidizing step using a low oxygen concentration gas containing steam in specific concentration at specific temperature. **CONSTITUTION:** As for a metallic oxide mainly comprising iron, a spinel compound having no dehydrating hole at all bored by heating step in an inert gas atmosphere after particle surfaces are coated with a mixture layer containing at least dihydric transition metallic compound is used. Next, a metallic iron produced by reducing this metallic oxide using a reducing gas is surface oxidized. As for this oxidizing step, the reduced metallic iron is oxidized at the temperature of 60-120 deg.C in an inert gas containing moisture content at the partial steam pressure of 20-50mmHg and 100-2500ppm of oxygen. This surface oxidizing step, despite a simple one, can notably enhance the oxidation resistance thereby enabling the manufacturing method of metal magnetic powder having excellent magnetic characteristics to be devised.

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(54)【発明の名称】 金属磁性粉末の製造方法

(57)【要約】

【構成】鉄を主体とする金属酸化物を還元性ガスにより還元し、得られる金属鉄を表面酸化処理して金属磁性粉末を製造する方法において、表面酸化処理が、還元後の金属鉄を水蒸気分圧 2 0 ~ 5 0 mmHg の水分と 1 0 0 ~ 2 5 0 0 ppm の酸素を含む不活性ガス中で、温度 6 0 ~ 1 2 0 °C で酸化するものであることを特徴とする金属磁性粉末の製造方法。

【効果】本発明の金属磁性粉末の製造方法によると、簡易な表面酸化処理により、耐酸化性が大幅に改良され、磁気特性にも優れる金属磁性粉末を得ることができる。

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## 【特許請求の範囲】

【請求項1】 鉄を主体とする金属酸化物を還元性ガスにより還元し、得られる金属鉄を表面酸化処理して金属磁性粉末を製造する方法において、表面酸化処理が、還元後の金属鉄を水蒸気分圧20～50mmHgの水分と100～2500ppmの酸素を含む不活性ガス中で、温度60～120℃で酸化するものであることを特徴とする金属磁性粉末の製造方法。

【請求項2】 鉄を主体とする金属酸化物が、針状晶の含水酸化鉄粒子の粒子表面に少なくとも2価の遷移金属化合物を含有する混合物層を被覆した後、不活性雰囲気中で加熱して得られる実質的に脱水孔の存在しないスピネル化合物である請求項1記載の製造方法。

【請求項3】 少なくとも2価の遷移金属化合物を含有する混合物層が、コバルト化合物とケイ素化合物および／またはアルミニウム化合物からなる層である請求項2記載の製造方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は磁気記録に用いられる金属磁性粉末の製造方法に関し、更に詳しくは、メタル粉前駆体を還元してメタル化した後の表面酸化安定化を特定濃度の水蒸気を含む低酸素濃度ガスを用いて、かつ特定の温度範囲で行うことにより、耐酸化性の優れた金属磁性粉末を製造する方法に関するものである。

## 【0002】

【従来の技術・発明が解決しようとする課題】 近年、各種の記録方式の発展は著しいものがあるが、中でも磁気記録再生装置の小型軽量化の進歩は顕著である。これにつれて磁気テープ・磁気ディスク等の磁気記録媒体に対する高性能化の要求が大きくなってきている。

【0003】 磁気記録に対するこのような要求を満足するためには高い保磁力と高い飽和磁化を有する磁性粉末が必要である。従来、磁気記録用の磁性粉末として一般には針状のマグネタイトやマグヘマイト又はこれらの磁性酸化鉄粉末をコバルトで変性したいわゆるコバルト含有酸化鉄が用いられているが、より高出力の媒体を得るためにはより高い保磁力・飽和磁化を持つ強磁性金属粉末いわゆるメタル磁性粉が用いられ始めている。

【0004】 このような金属磁性粉末の製造方法としては、種々の方法が提案されているが、経済的な優位性から、一般的には、針状のゲーサイトまたはこれを加熱脱水して得られる酸化鉄粒子を水素等の還元性ガス雰囲気中で加熱して金属鉄にまで還元する方法が用いられている。

【0005】 しかしながら、このようにして得られた金属磁性粉末には大きな問題が存在する。すなわち、金属磁性粉末は化学的に不安定であり時間の経過と共に飽和磁化が減少するという欠点がある。この欠点の解決のために種々提案がなされており、例えば、溶剤中での表面

酸化（例えば特開昭59-16901号公報、特開昭59-170201号公報）や、気相中で多段階に温度を変えながら酸化を行う方法（特開平1-21002号公報）が提案されているが、未だ十分な性能が得られていない。また水蒸気を併用しながら高温（200～600℃）で酸化を行う方法（特開昭60-26602号公報）も提案されているが、後で述べるように静磁気特性の劣化が生じるため望ましい方法とは言えない。

【0006】 本発明の目的は、かかる課題を解決すべく、簡易な表面酸化処理により、耐酸化性が大幅に改良され、磁気特性にも優れる金属磁性粉末の製造方法を提供することにある。

## 【0007】

【課題を解決するための手段】 本発明者らは、前記の目的を達成するため、鉄を主体とする金属酸化物を還元して得た金属磁性粉末の酸化安定化について検討を行なった結果、表面酸化処理を特定濃度の水蒸気を含む低酸素濃度ガスを用い、特定の温度で行うことにより、金属磁性粉末の耐酸化性を大幅に改良することができることを見だし、本発明の完成に至った。

【0008】 即ち、本発明の要旨は、鉄を主体とする金属酸化物を還元性ガスにより還元し、得られる金属鉄を表面酸化処理して金属磁性粉末を製造する方法において、表面酸化処理が、還元後の金属鉄を水蒸気分圧20～50mmHgの水分と100～2500ppmの酸素を含む不活性ガス中で、温度60～120℃で酸化するものであることを特徴とする金属磁性粉末の製造方法に関する。また、本発明の製造方法において、鉄を主体とする金属酸化物が、針状晶の含水酸化鉄粒子の粒子表面に少なくとも2価の遷移金属化合物を含有する混合物層を被覆した後、不活性雰囲気中で加熱して得られる実質的に脱水孔の存在しないスピネル化合物を用いると本発明の効果は特に有効である。

【0009】 本発明に用いられる鉄を主体とする金属酸化物の軸比、大きさは一般的に金属磁性粉末の原料として通常用いられるものであれば良く、特に制限はない。さらに、磁気特性のコントロールや分散性その他の特性の改良のために種々の金属元素を含むものであっても差し支えない。鉄を主体とする金属酸化物のメタルへの還元は、一般的に用いられる公知の還元法が適用され、例えば水素気流中で350～550℃に2時間以上保つ方法が挙げられる。

【0010】 得られたメタル粉は非常に活性が強く酸化を受けやすいために、本発明の製造方法では、以下のような表面酸化処理が行われる。即ち、本発明における表面酸化処理方法は、通常、水蒸気分圧20～50mmHgの水分および100～2500ppmの酸素を含む不活性ガスを通じる事により行われ、好ましくは、水蒸気分圧20～50mmHgの水分および200～500ppmの酸素を含む不活性ガスが用いられる。水蒸気分圧

が20mmHgより低いと水蒸気を含むことの効果が見られなくなり、50mmHgより高いとかえって耐酸化性が不良となる。また、酸素濃度は2500ppmを越えると、局部的な発熱のためと考えられるが、磁気特性の低下が起こるため好ましくない。酸素濃度が低い場合は特に大きな問題はないが、所定の厚さの酸化膜を得るまでの時間が長くなり作業性の面からは100ppm程度が下限と考えられる。

【0011】さらに、酸化を行う際の酸化温度も重要であり、通常60～120℃、好ましくは70～90℃で行う必要がある。即ち、温度が低すぎると配管内での結露等により所定の水蒸気分圧を維持することが困難となり、逆に高すぎると共存水蒸気の効果の不十分となり十分な耐酸化性が得にくく、磁気特性の低下をともなう等の問題が発生するためである。処理の時間は、表面酸化が実質的に進まなくなるまでの時間を設定すればよく、例えば入口酸素濃度にもよるが出口酸素濃度と入口酸素濃度の差が約30ppm以下になるようにすればよい。一般的には、70℃で酸素濃度250ppmの条件で行う場合、30時間程度行えばよい。このように本発明における表面酸化処理方法は、簡易な方法であるにもかかわらず、耐酸化性が大幅に改善される。

【0012】本発明の製造方法においては、鉄を主体とする金属酸化物が、針状晶の含水酸化鉄粒子の粒子表面に少なくとも2価の遷移金属化合物を含有する混合物層を被覆した後、不活性雰囲気中で加熱して得られる実質的に脱水孔の存在しないスピネル化合物である場合がより好ましいが、このようなスピネル化合物は、次のようにして得ることが出来る。

【0013】2価の遷移金属化合物としては、Co、Fe、Zn、Cu、Cr、Ni化合物などが挙げられ、特に制限されるものではない。2価の遷移金属化合物とともに混合物層を構成する他の化合物としては、通常ケイ素、アルミニウム、スズ、チタン化合物など公知の化合物が用いられ、例えばコバルト化合物とケイ素化合物の混合物からなる層、コバルト化合物とアルミニウム化合物の混合物からなる層、あるいはコバルト化合物、ケイ素化合物およびアルミニウム化合物の3種の化合物の混合物からなる層などが挙げられる。

【0014】2価の遷移金属化合物を含有する混合物層には、2価の遷移金属化合物をゲーサイト中の鉄原子に対する重量比として、通常3～25%、好ましくは7～20%含有している。これは、2価の遷移金属の量が多すぎても少なすぎても所望の特性が得られなくなるためである。また、混合物層を構成する他の化合物、例えばケイ素化合物、アルミニウム化合物などのケイ素およびアルミニウム原子は、同様にゲーサイト中の鉄原子に対する重量比として、通常0.2～2%、好ましくは0.5～1%を含有している。また、2価の遷移金属化合物と混合物層を構成する他の化合物との原子重量比は、通

常10:1～20:0.5である。

【0015】このような2価の遷移金属化合物を含有する混合物層を針状含水酸化鉄粒子表面へ形成する方法は、溶液状態からの不溶物の析出、コロイド状化合物等の沈着等に用いられる公知の方法により行なわれる。その具体例として、例えばコバルト化合物とケイ素化合物の混合物からなる層を形成させるには、3号ケイソーを添加後、硫酸コバルト水溶液にて系のpHを7付近とし、コバルト化合物とアルミニウム化合物の混合物からなる層を形成させるには、硫酸アルミニウム水溶液と硫酸コバルト水溶液を同時添加した後、アルカリ水溶液にて系のpHを7付近とし、またコバルト化合物、ケイ素化合物およびアルミニウム化合物の3種の化合物の混合物からなる層を形成させるには、3号ケイソーを添加後、硫酸コバルトおよび硫酸アルミニウム水溶液にて系のpHを7とし、その後アルカリ水溶液にて系のpHを10とするなど、通常、ゲーサイトのスラリーに硫酸塩等の酸性水溶性化合物水溶液を加え、次いでアルカリ性水溶液により系のpHを調節することにより不溶性酸化物ないし水和酸化物を析出させる方法が挙げられる。

【0016】本発明で言うスピネル化合物とは酸化鉄を主とした酸化物であり、面間隔2.97±0.05、2.53±0.05、2.10±0.05オングストロームに相当する位置にX線回折の主要ピークを有するものをさしている。

【0017】一般に、ゲーサイトを空気中で加熱脱水すると脱水孔が生じやすくなるが、この脱水孔は電子顕微鏡により観察することができる。脱水孔の有無を簡単に判断する方法としては、流動式比表面積自動測定装置（フローソープ2300形、島津製作所製）により測定された粒子の比表面積値と脱水孔の有無とは相関がみられるので、脱水孔の有無を比表面積値から得られる減少率を用いて判断することができる。即ち、本発明で言う実質的に脱水孔の存在しないスピネル化合物とは、高温加熱処理する前後での粒子の比表面積の減少率が10%以上のスピネル化合物であり、10%未満のものは脱水孔がみられるものである。ここで減少率は次式により求められる。

減少率＝(熱処理前の比表面積－熱処理後の比表面積)／熱処理前の比表面積

【0018】本発明の方法において、このような実質的に脱水孔の存在しないスピネル化合物を形成させるには、針状晶の含水酸化鉄粒子を不活性ガス気流中で含水酸化鉄粒子を高温加熱処理することにより容易になし得る。この処理は、針状晶の含水酸化鉄粒子表面に前記のようにして少なくとも2価の遷移金属化合物を含有する混合物層を被覆した後になされる。この場合、不活性ガスとしては特に制限されることはなく、通常窒素ガス、アルゴンガスなどが用いられるが、安価である点から好ましくは窒素ガス気流中で行うのが良い。



【0019】高温加熱処理の温度範囲は、通常400～700℃であり、好ましくは450～600℃である。400℃より低いとヘマタイトのままであるため、不活性ガス気流中の処理であっても脱水孔が生じやすくなり、700℃より高いと粒子が融着を起こしやすくなるので、好ましくない。加熱時間は、加熱温度にもよるが通常0.5～4時間、好ましくは1～2時間である。

【0020】このような、高温加熱処理を特開昭63-61413号公報に記載されているように空気中で行うとスピネル化合物は形成されず、脱水孔の残ったヘマタイトを形成するに留まり、水素気流中での還元時に切断が生じてしまい針状性を保持しなくなり、目的とする性能をもつ金属磁性粉末を得ることができなくなる恐れがあるので注意を要する。

【0021】本発明の製造方法は、以上のようなスピネル化合物を好適に用いることができるが、本発明では必要に応じて前記の混合物層とは別に更にその他の化合物による被覆を行ったものを用いることもできる。例えば、加熱還元時において金属磁性粉末の粒子間の焼結を防止するため、粒子の最外殻にケイ素、アルミニウムなどの公知の化合物を沈着させることができる。最外層であるケイ素化合物、アルミニウム化合物層は単独あるいは両者の併用の形で形成されるが、なかでもケイ素化合物層形成後、アルミニウム化合物層を形成したものをを用いると、最終的に得られる金属磁性粉末の性能が特に優れる。

【0022】この場合のケイ素および／またはアルミニウム化合物層の形成はゲーサイト中の鉄原子に対するケイ素および／またはアルミニウムの合計の重量比として1～10%、好ましくは2～6%である。これは、ケイ素、アルミニウムの合計が10%よりも多すぎると得られる金属磁性粉末の飽和磁化がかえって低くなり望ましくないためである。また、1%未満では最外層としてこれらの被覆を行なった効果が得られないからである。

【0023】このようにして得られた2価の遷移金属化合物を含有する混合物層、ケイ素またはアルミニウム化合物層を有するゲーサイトを前記のように不活性ガスとして、例えば窒素気流中で400～700℃に加熱すると実質的に脱水孔の存在しないスピネル化合物に変換でき、本発明に用いることができる。

【0024】以上のようにして得られる耐酸化性、磁気特性に優れた金属磁性粉末を含有する磁気記録媒体の製造は、常法に準じて行うことができる。すなわち、この金属磁性粉末を、結合剤樹脂、有機溶剤およびその他の必要成分とともに分散混合して磁性塗料を調製し、この

磁性塗料をポリエステルフィルムなどの基体上に、ドクターブレード法、グラビア法、リバース法、ロール塗りなど任意の手段で塗布し、必要により磁場配向後、乾燥するなどの方法で行なう。

【0025】

【実施例】以下、実施例、比較例により本発明をさらに詳しく説明するが、本発明はこれらにより何等制限されるものではない。

【0026】実施例1

10 反応槽の外部にパイプライン型分散機マイルダー（荏原製作所製）を設置した循環ラインを設けた装置を用い、ゲーサイト（長軸径：0.18μm、軸比：8）500gを、ポイズ530（花王株式会社製）15g（対粉3%）をイオン交換水10リットルに添加した溶液に約1時間分散した。マイルダーによる分散を続けながら、3号ケイソー（SiO<sub>2</sub>分29%）17.2gを加えた。ついで、硫酸コバルト七水和物270gを1000mlのイオン交換水に溶解した水溶液をpH6.5まで滴下して、表面にSi/Co混合物層を被着せしめた後、残りの硫酸コバルト水溶液を滴下し、1.2mol/リットルNaOH水溶液を滴下し、pHを10とした。その後、イオン交換水を用いて洗浄液の電気伝導度が100μS/cm以下になるまで洗浄した。さらに、これに、ポイズ530（15g）を加え再分散し、3号ケイソー（SiO<sub>2</sub>分29%）69gを加え、1時間後希硝酸を滴下し、pHを6.5にして、ケイ素化合物層を被着せしめた。最後に、この懸濁液に濃度2NのNaOH水溶液172mlを添加した後、ただちに、硫酸バンド（Al<sub>2</sub>O<sub>3</sub>分9.3%）34gをイオン交換水165gに溶解した水溶液を滴下し、アルミニウムの水酸化物の層を被着せしめ、この沈澱を水洗、濾過、乾燥した。

30 【0027】以上のようにして得たメタル前駆体を48～64メッシュに整粒し、内径62mmの流動槽炉でガス線速度7cm/秒の窒素気流中500℃で1時間加熱処理を行なった。次いで水素気流中500℃で6時間還元した。還元終了後、80℃で250ppmの酸素を含む水蒸気分圧34mmHgの窒素ガスをガス線速度7cm/秒で通気し、出口酸素濃度が230ppm以上になるまで表面の酸化を行なった。その後、窒素ガス中で乾燥し、本発明品である金属磁性粉末1を得た。得られた金属磁性粉末の特性を他の例（実施例2～3、比較例1～3）とともに表1に示す。

40 【0028】

【表1】

	金属磁性 粉末No	H c (Oe)	$\sigma_s$ (emu/g)	$\sigma_r/\sigma_s$	$\sigma_{s'}$ (emu/g)	$\sigma_{s'}/\sigma_s$ (%)
本 発 明 品	1	1600	120	0.51	115	96
	2	1610	123	0.52	116	94
	3	1600	123	0.51	116	94
比 較 品	1	1600	121	0.51	107	88
	2	1580	119	0.51	105	88
	3	1500	115	0.47	—	—

注)  $\sigma_{s'}$  : 60℃/90%RH保存1週間後の $\sigma_s$

【0029】実施例2

実施例1と同様にメタル前駆体の還元までを行なった後、70℃で250ppm酸素を含む水蒸気分圧34mmHgの窒素ガスをガス線速度7cm/秒で通気し、出口酸素濃度が230ppm以上になるまで表面の酸化を行なった。その後、窒素ガス中で乾燥し、本発明品である金属磁性粉末2を得た。

【0030】実施例3

実施例1と同様にメタル前駆体の還元までを行なった後、70℃で500ppmの酸素を含む水蒸気分圧34mmHgの窒素ガスをガス線速度7cm/秒で通気し、出口酸素濃度が470ppm以上になるまで表面の酸化を行なった。その後、窒素ガス中で乾燥し、本発明品である金属磁性粉末3を得た。

【0031】比較例1

実施例1と同様にメタル前駆体の還元までを行なった後、80℃で250ppmの酸素を含み水蒸気を含まない窒素ガスをガス線速度7cm/秒で通気し、出口酸素濃度が230ppm以上になるまで表面の酸化を行ない、金属磁性粉末(比較品1)を得た。

【0032】比較例2

実施例1と同様にメタル前駆体の還元までを行なった後、80℃で250ppmの酸素を含む水蒸気分圧100mmHgの窒素ガスをガス線速度7cm/秒で通気し、出口酸素濃度が230ppm以上になるまで表面の

酸化を行なった。その後、窒素ガス中で乾燥し、表面を酸化した金属磁性粉末(比較品2)を得た。

【0033】比較例3

実施例1と同様にメタル前駆体の還元までを行なった後、150℃で250ppmの酸素を含む水蒸気分圧34mmHgの窒素ガスをガス線速度7cm/秒で通気し、出口酸素濃度が230ppm以上になるまで表面の酸化を行なった。その後、窒素ガス中で乾燥し、表面を酸化した金属磁性粉末(比較品3)を得た。

【0034】以上の様に、実施例1~3では高保磁力(Hc)、高角型比( $\sigma_r/\sigma_s$ )をもつ金属磁性粉末が得られ、得られた金属磁性粉末は、60℃/90%RH雰囲気下で1週間保存した後も高い飽和磁化( $\sigma_{s'}$ )を保ち、耐酸化性が優れることがわかる。一方、比較例1、2で得られた金属磁性粉末は、磁気特性は十分であるが60℃/90%RH雰囲気下で1週間保存した後には飽和磁化( $\sigma_{s'}$ )が低く、耐酸化性が劣る。また、比較例3では酸化温度が高いため磁気特性の劣化がみられる。

【0035】

【発明の効果】本発明の金属磁性粉末の製造方法によると、簡易な表面酸化処理により、耐酸化性が大幅に改良され、磁気特性にも優れる金属磁性粉末を得ることができる。